



Short communication

Nickel phosphate molecular sieve as electrochemical capacitors material



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HIGHLIGHTS

- Microporous nickel phosphate VSB-5 was employed as a new class of electrochemical capacitors material.
- VSB-5 exhibited a high specific capacitance of $\sim 2740 \text{ F g}^{-1}$ at a charge and discharge current density of 3 A g^{-1} .
- There was no significant reduction in Coulombic efficiency after 3000 cycles at 30 A g^{-1} .

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ABSTRACT

The nickel phosphate molecular sieve VSB-5 as an electrode material for supercapacitors is investigated by cyclic voltammetry (CV) and chronopotentiometry in alkaline media. The VSB-5 shows high specific capacitance and excellent cycling stability. The specific capacitance of VSB-5 is 2740 F g^{-1} at a current density of 3 A g^{-1} and there is no significant reduction in Coulombic efficiency after 3000 cycles at 30 A g^{-1} . In comparison with mesoporous nickel phosphate NiPO, porous nickel hydroxide and mesoporous nickel oxide, this remarkable electrochemical performance of VSB-5 will make nickel phosphate material a promising new electrode material for high performance supercapacitors.

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1. Introduction

Electrochemical capacitors (ECs) have been of great interest, due to their high power density, rapid charge/discharge processes and long-term cycling stability [1]. They are considered as main next-generation energy storage systems. With the development of human society, high fuel prices and the global warming crisis forced people to develop new energy storage technologies for clean and renewable energy sources [2–4]. Generally, there are two types of ECs, electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. The capacitance of EDLCs arises from charge separation between electrode and electrolyte interface. While, the capacitance of pseudocapacitors is mainly from the reversible faradaic redox

reaction between the active material and electrolyte at the electrode surface. The pseudocapacitors have higher energy density and specific capacitance than EDLCs [5,6]. The most common pseudocapacitors materials are the hydroxides and oxides, for instance, Ni(OH)_2 [7–9], RuO_2 , MnO_2 , Co_2O_3 , V_2O_5 and NiO materials [10–16]. Among these materials, hydroxide and oxide of nickel are regarded as good candidates owing to its low cost, lower toxicity, easy synthesis and high theoretical specific capacity.

A zeolitic nickel phosphate VSB-5 with pore size of $\sim 1.0 \text{ nm}$, first reported by Cuillou et al., showed high activity and high selectivity in the epoxidation of cyclic olefins [17]. Recently, we have reported a novel electro-oxidation catalyst, a mesoporous nickel phosphate NiPO, which is an aggregate of hollow nanotubes. Owing to the better diffusion of reactant molecules in the mesopores, NiPO modified glassy carbon electrode (GCE) showed higher activity in the electro-oxidation of methanol [18,19]. These studies clew us developing the phosphate compounds for potential electrochemical capacitors materials. Porous nickel phosphates

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combine the advantages of redox catalytic property of nickel with large surface area and open diffusion accesses. Accordingly, their performance in electrochemical capacitors seems to be expectable. In the present work, VSB-5 and NiPO were employed to fabricate electrodes for electrochemical capacitors. They showed high specific capacitance and excellent cycling stability.

2. Experimental

2.1. Reagents

Nafion (5 wt.% ethanol solution) was purchased from Alfa Aesar, and diluted to 0.1 wt.% with doubly distilled water in use. Hexadecyltrimethyl ammonium bromide (CTAB), tetramethylammonium hydroxide (TMAOH), H₃PO₄ (85%) and Ni(NO₃)₂·6H₂O were products of Tianjin Kermel Chemical Co. in analytical grade. The surfactant copolymer poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide), commercially known as Pluronic (P123 EO₂₀–PO₇₀–EO₂₀). Sodium borohydride was obtained from Sino-pharm Chemical Reagent Co., Ltd. Polytetrafluoroethylene (PTFE, 60 wt. % water suspension) was from Aladdin. Other chemicals were all analytical reagents from Beijing Chemical Company. All stock solutions used in this work were prepared with deionized water resistively not less than 18.2 MΩ cm.

2.2. Synthesis of materials

The nickel phosphate VSB-5 was synthesized by hydrothermal method using nickel chloride as nickel source, phosphoric acid as phosphorus source without any template. A starting gel with molar composition 0.5H₃PO₄:1.0NiCl₂:3.0NH₃:100H₂O was prepared at 333 K (pH = 8–10) and kept for 5 h. After sufficient mixing, put the mixture into PTFE-lined autoclave and crystallized at 453 K for 5 d. Then the mixture was washed by centrifugation, dried to give VSB-5 raw powder. The NiPO was prepared by the same method as described in Ref. [18]. Ni(OH)₂ was based on a self-assembly between a triblock copolymer template P123 and two precursors (sodium borohydride and nickel species) in a flask. 40 ml solution of Ni(NO₃)₂·6H₂O (8.6 g) was put into the 400 ml solution of P123 (4 g), and then stirred at 313 K for 2 h. When the temperature dropped to ambient temperature, the 20 ml sodium borohydride (1.5 g) solution was added into the mixture. After 2 h, add the same quantity of sodium borohydride solution to the mixture during 10 min. After 200 min, light green sediments were formed. Finally, the product was collected by filtration, washed with distilled water and ethanol several times, and dried at 333 K in vacuum for 24 h. We got the mesoporous NiO nanoflowers by calcination the Ni(OH)₂ at 873 K for 4 h with the heating rate 10 K min⁻¹.

2.3. Preparation of nickel electrodes and electrochemical measurements

A three electrode system was used. Ag/AgCl electrode filled with saturated potassium chloride was used as reference electrode and platinum foil was used as counter electrode with 1 M aqueous solution of KOH as electrolyte. The working electrode was prepared as follows: approximately 0.5 mg (1.2, 3.3 and 5.1 mg as control mass) material was first mixed with polytetrafluoroethylene (PTFE) and acetylene black at a given weight ratio (90:5:5). And then dispersed in ethanol, the suspension was drop-dried into a 1 cm × 1 cm Ni foam (2 mm thick, 90 ppi, 95% porosity) at ambient temperature. Then the foam dried at 333 K for 12 h, then pressed at 10 MPa. Before testing, the compact foam was immersed in the electrolyte for 24 h.

The steady-state cyclic voltammograms (CVs) were recorded on a CHI660D electrochemical workstation (CHI, Shanghai) at 298 K.

$$C = \frac{\int I dt}{m \Delta V}$$

The above formula was employed as equation for calculating average specific capacitance values from the CV curves. Where I means the oxidation or reduction current, m indicates the mass of the active electrode material, dt indicates time differential, and ΔV is the voltage range of one sweep segment. And there is another method for calculating the specific capacitance values from the galvanostatic charge and discharge curves as the following formula:

$$C = \frac{I \Delta t}{m \Delta V}$$

While, where I represents charge or discharge current, Δt indicates the time for a full charge or discharge, ΔV is the voltage change after a full charge or discharge and m is the mass of the active material.

2.4. Characterization

Nitrogen adsorption and desorption measurements were carried out at 77 K on a Micromeritics ASAP 2010 analyzer. Prior to the measurements, NiPO sample was outgassed at 373 K for over 4 h, VSB-5, Ni(OH)₂ and NiO samples at 573 K for over 4 h. The specific surface area was calculated using the BET (Brunauer, Emmett, and Teller) equation. Pore size distribution was calculated by the BJH (Barrett, Joyner, and Halender) method using the adsorption branches of the isotherms.

3. Results and discussion

As to VSB-5, the specific surface area is high to 226 m² g⁻¹. The specific surface area of control material NiPO, Ni(OH)₂ and NiO is 274, 400 and 200 m² g⁻¹ by BET measurements, respectively. The specific surface area of these as-prepared materials is still relatively high in the corresponding field, respectively. Nickel phosphate framework is composed of the elements Ni, P, O. The VSB-5 is microporous zeolite crystal with pore size of 1.02 nm and the structured one-dimensional channel consists of 24 Ni₆ octahedra. While the NiPO is a kind of mesoporous material with pore size of ~3 nm. NiPO consists of closely packed short tubes like worms. The essential differences is that VSB-5 is a kind of microporous zeolite crystal with regular pores and high stability of the crystal structure but NiPO is a kind of amorphous mesoporous material whose structure stability is not better than VSB-5. The electrochemical properties of VSB-5 and the control material NiPO are evaluated by means of steady-state cyclic voltammogram (CV) in 1 M KOH solution at a potential scan rate of 5 mV s⁻¹ (Fig. 1(A)). The shapes of the CV curves indicate that the capacity is mainly associated with the pseudocapacitive properties of the materials and it is based on a redox mechanism, whose capacitance characteristics are quite different from electric double layer capacitance, where the CV curve is normally close to an ideal rectangular shape [15]. There are two pairs of redox peaks (a/c and b/d) observed. These redox peaks may presumably come from the redox processes of skeleton nickel phosphate (Ni(II)PO₄/Ni(III)PO₄) and surface nickel hydroxide (Ni(OH)₂/NiOOH). Not only the peak current but also the capacity according to the CV curve, the performance of VSB-5 is better than that of NiPO. Besides the nickel phosphate, there are also two pairs of redox peaks for NiO from the redox processes of nickel oxide (NiO/NiOOH) and nickel hydroxide (Ni(OH)₂/NiOOH) [20]. This is consistent with some literature reports [21]. By contrast CV curve of nickel hydroxide (Fig. 1(B)), we could find that the CV curve of the

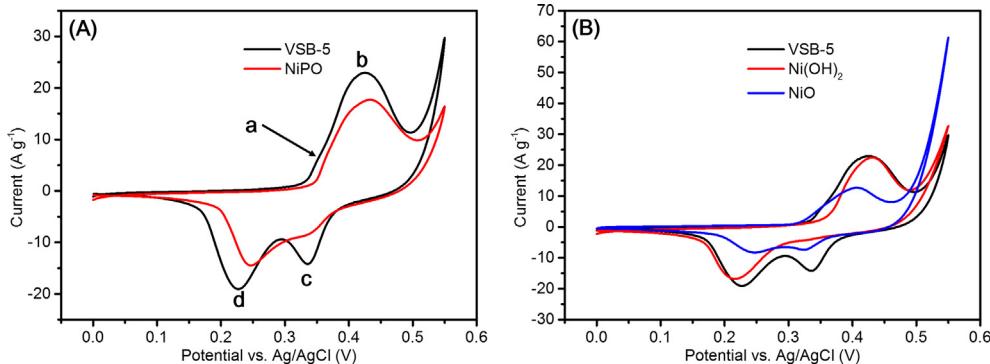


Fig. 1. CV curves of VSB-5 and NiPO materials (A) and the control materials Ni(OH)₂ and NiO (B) at 5 mV s⁻¹.

pure VSB-5 sample had an anodic peak (344 mV) and a corresponding cathodic peak (335 mV) assigned to the Ni(II)PO₄/Ni(III)PO₄ redox couple in the framework with another redox peaks of Ni(OH)₂/NiOOH corresponding to 0.425 V/0.228 V. The NiPO material has the similar characteristic except slight shift of the redox peaks to higher potential.

We have employed large mass of VSB-5 (5.1 mg) for electrochemical measurements. The specific capacitance of 5.1 mg material was 96% and 84% that of 0.5 mg material at 5 mV s⁻¹ and 10 mV s⁻¹, respectively. Obviously, although there is microbalance with hundred thousandth accuracy, a relatively larger amount of catalyst can theoretically reduce system error. The purpose of that we try to choose a small amount of materials is for obtaining more accurate capacitance characteristics of the porous nickel phosphate materials. The reason is that the porous material VSB-5 requires full activation and infiltration of electrolyte. It is more difficult to activate the active substance for the porous nickel phosphate crystals because of the unique structure. We know that there are two active substances, one is the Ni(OH)₂ on the pore surface from the reaction between Ni(II) and the electrolyte NaOH, the other is the reserved backbone nickel phosphate. On the same collector area, the less of the amount of catalyst, the easier being activated. As shown in Fig. 2(A), when the material was 1.2 mg, there is obvious redox peaks (a/c), not to mention that of 0.5 mg VSB-5. However, when the amount of the catalyst is increased to 5 mg, the redox peaks (a/c) directly disappear. As to the difficult activated VSB-5, because of the accumulation of large mass of materials (5.1 mg) in collector (1 × 1 cm), the longer time and more fully invasion in NaOH

solution, the greater of the capacitance and there is nearly no contribution from redox peaks (a/c) of Ni(II)PO₄/Ni(III)PO₄ (Fig. 2(B)). In fact, there is microbalance with hundred thousandth accuracy (0.01/0.1 mg) which could be used for accurately weighing 0.5 mg sample. Relative to the weighing system error, and we can even use more precise equipment to eliminate systematic errors, whether completely activation of the electrode itself looks more important, so we have chosen a smaller mass of materials for investigation.

Fig. 3(A) shows galvanostatic discharge curves of the as-prepared materials at a charge and discharge current density of 3 A g⁻¹. In Fig. 3(B), VSB-5 shows a specific capacitance as high as ~2740 F g⁻¹ based on mass of VSB-5. The NiPO materials show a specific capacitance as high as ~2285 F g⁻¹ based on mass of NiPO, still a high specific capacity. The specific capacity of Ni(OH)₂ and NiO is ~2275 F g⁻¹ and ~1309 F g⁻¹ based on mass of corresponding material, respectively. Overall, there is the highest specific capacity of VSB-5 among that of as-prepared materials containing nickel. As shown in Fig. 4(A, B), the specific capacitance of VSB-5 is still as high as ~1625 F g⁻¹ even at a high charge and discharge current density of 48 A g⁻¹. The VSB-5 shows higher capacitance than NiPO. Although the both materials have almost the same specific surface area, in the course of the synthesis of NiPO, the template hexadecyltrimethyl ammonium bromide (CTAB) was necessary. No matter how clean for washing, the template will inevitably adsorb in the pores surface of NiPO. However, there is not the problem for VSB-5 because of no template for synthesis of VSB-5. Another reason is probably that because the

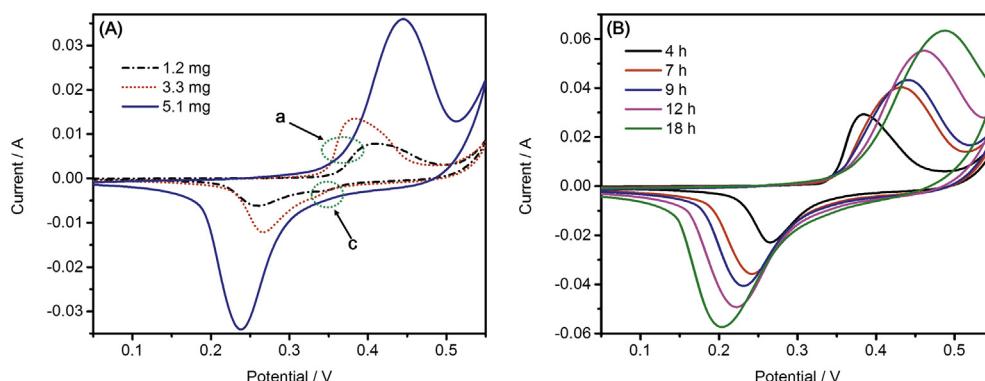


Fig. 2. CV curves of different amounts of VSB-5 after infiltration for 12 h in NaOH solution at scan speed of 5 mV s⁻¹ (A). The CVs of VSB-5 (5.1 mg) after infiltration for different time in NaOH solution at scan speed of 10 mV s⁻¹ (B).

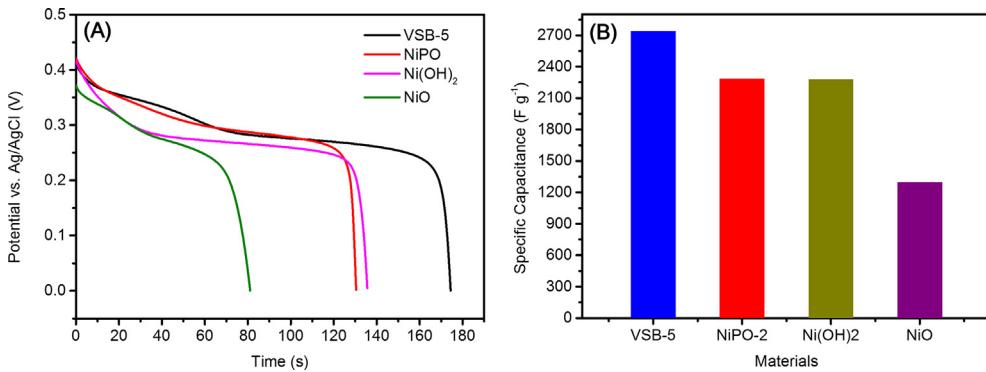


Fig. 3. Galvanostatic discharge curves (A) and the corresponding average specific capacitance (B) of as-prepared materials at a discharge current density 5 A g^{-1} .

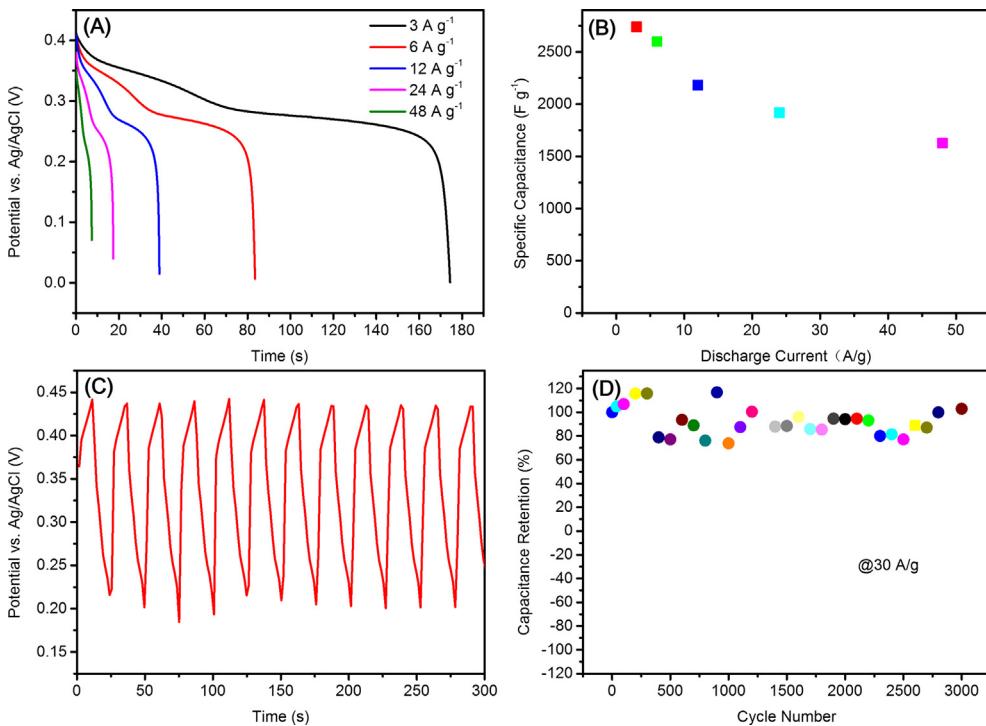


Fig. 4. Galvanostatic discharge curves (A) and the corresponding average specific capacitance (B) of VSB-5 at various discharge current densities. Galvanostatic charge and discharge curves (C) and the corresponding average specific capacitance retention versus cycle number (D) of VSB-5 at a discharge current density of 30 A g^{-1} .

VSB-5 structure is more stable than NiPO. After all, the structure of nickel phosphate crystal should be more stable than that of amorphous nickel phosphate.

Importantly, the Coulomb efficiency is nearly 100% for each cycle of charge and discharge (Fig. 4(C)). There was no obvious capacitance decrease observed over 3000 cycles of charge and discharge at a high current density of 30 A g^{-1} (Fig. 4(D)). Though there is no significant reduction in specific capacitance after 3000 cycles. The specific capacitance changed between 80% and 120%. We suppose there are two main reasons because the porous material VSB-5 requires full activation and infiltration of electrolyte. It is more difficult to activate the active substance for the porous nickel phosphate crystals because of the unique structure. Furthermore, the Ni(II) on the surface of VSB-5 will produce active Ni(OH)₂ from the reaction between Ni(II) and NaOH, and at the same time, the Ni(OH)₂ will conversely be converted to nickel phosphate, too. In the charge-discharge process, where Ni(OH)₂ and Ni(II)PO₄ are transformed into each other and the apparent specific capacitance of the two kind active ingredients is different.

So there will be some in the apparent capacitance value. The other reason is that there will be some reconstruction of the pore structure of VSB-5, in the charge-discharge process. These results reveal the high specific capacitance and remarkable rate capability of the VSB-5 material for high-performance electrochemical capacitors.

4. Conclusions

Porous nickel phosphates were employed as electrode materials for the electrochemical capacitors. We have demonstrated that nickel phosphate electrodes exhibited excellent electrochemical capacitance and remarkable rate capability, especially, VSB-5, whose electrochemical capacitance was high to 2740 F g^{-1} and 1625 F g^{-1} based on mass of VSB-5 at a charge and discharge current density of 3 A g^{-1} and 48 A g^{-1} , respectively. There was no obvious capacitance decrease over 3000 cycles at 30 A g^{-1} implying the excellent cycling stability of VSB-5. In short, comparing to nickel hydroxide and nickel oxide, nickel phosphate also has a good

performance of the electrochemical capacitor, even better. Thus, the nickel phosphate material is a new promising class of electrode material for electrochemical supercapacitors.

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